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## PATENT SPECIFICATION

NO DRAWINGS.

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## COMPLETE SPECIFICATION.

## Chromising Ferrous Metal Substrates.

We, ASSOCIATED CHEMICAL COMPANIES LIMITED, a British Company of Beckwith Knowle, Harrogate, Yorkshire, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the chromising of ferrous metal substrates.

In the chromising of ferrous metal substrates a chromous halide vapour is presented to the surface of the substrate at a high temperature. The chromous halide interacts with the iron of the substrate to yield chromium metal and ferrous halide. The deposited chromium then diffuses into the surface of the substrate forming a chromium/iron alloy surface which is corrosion resistant.

In one type of chromising process used hitherto the article to be chromised is introduced into a furnace which is then purged of air by the passage therethrough of a non-oxidising gas and the temperature is raised to the operating temperature which is in excess of 840°C and usually of the order of 1000°C. Once the operating temperature has been reached a hydrogen halide is incorporated into the gas stream passing through the furnace. The gases containing hydrogen halide are then passed over a source of chromium, which may be sited either in a separate furnace or in the furnace containing the workpiece, to form the chromous halide required for chromising. In an alternative method it has been proposed to apply a compacted coating of chromium powder to the workpiece which is then placed in a furnace, heated to the operating temperature and chromised by maintaining at this temperature, optionally in the pre-

sence of a hydrogen halide contained in the non-oxidising gas-stream which is again continuously passed through the furnace.

Another method for achieving chromising is to pack the workpiece in a powder mixture containing an ammonium halide and powdered chromium or an alloy thereof and to heat the loaded furnace to the operating temperature of at least 900°C. In this process the ammonium halide decomposes to yield a hydrogen halide which reacts with the chromium present to form the chromous halide required. It is usual to carry out this method of chromising in a sealed furnace and not to pass a gas stream therethrough.

In these methods the ferrous halide, which is liberated from the surface of the workpiece during chromising, vapourises and forms part of the furnace atmosphere. Where a non-oxidising gas is passed continuously through the furnace substantially all of this ferrous halide is removed from the furnace. This represents a considerable loss of halogen from the system which might otherwise have taken part in the chromising process. In order to overcome this loss it has been customary in the commonly used processes to recycle the furnace off-gases over the source of chromium again. Where this is done the ferrous halide interacts with the chromium source to yield chromous halide which is used in the chromising process. However, the source of chromium gradually accumulates iron therein. As the proportion of iron increases the rate of pick up of chromium therefrom decreases. Since the surface of a chromised ferrous metal substrate normally contains 30–40% chromium metal, it follows that, when the chromium available on the surface of the source has dropped to this level, chromising ceases. In practice it is necessary to discard

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the source before this stage is reached in order to secure an acceptable rate of chromising. Thus, such processes are compromises between wastage of halogen and usage of chromium and whilst permitting a more economic usage of halogen necessitate discarding a substantial proportion of the chromium employed.

In the chromising process wherein the workpiece is packed with a powder containing ammonium halide and chromium, substantially all the halogen fed to the furnace is utilised in the chromising process by reaction of the ferrous halide formed with the chromium in the pack forming more chromous halide, which in turn reacts with the substrate surface producing more ferrous halide. The halogen is thus used repeatedly in the reactions involving transfer of chromium from the pack to the substrate and iron from the substrate to the pack. However, the chromium source again becomes contaminated with iron. Therefore, in order to secure satisfactory chromising it is necessary to use an excess of chromium, this excess being removed with the powdered packing at the end of the process.

According to the present invention a chromium coated substrate is heated in a furnace through which is passed a stream of a non-oxidising gas containing a hydrogen halide to a temperature of the order of 600°C, which is below that at which chromising takes place. After the halogen required for the chromising process has been fixed on to the surface of the substrate, the gas flow is stopped. The substrate is subsequently heated to the temperature at which chromising takes place. We find that by using this procedure substantially all the halogen and chromium fed to the furnace are utilised in the chromising process. The process of the invention also has the important result that it makes it possible to carry out chromising at temperatures of the order of 800°C which are substantially lower than the temperature hitherto necessary.

Accordingly, the present invention provides a process for the chromising of ferrous metal substrates which comprises:

1. applying a porous adherent coating which contains chromium and optionally other metals as well to a ferrous metal substrate;
2. heating the coated substrate in a stream of a non-oxidising gas containing a hydrogen halide to a temperature which is such that the hydrogen halide reacts with the surface of the coated substrate and yet is below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation; and

3. subsequently stopping the flow of gas and heating the coated substrate to a temperature of at least 750°C for sufficient time to cause a coating of the desired thickness and composition to be formed.

We believe that the mechanism by which this process enables effective chromising to be achieved using substantially all the chromium in forming the coating and the minimum amount of halogen is as follows. During the period when the hydrogen halide is introduced into the furnace, this is fixed on the substrate surface as a mixture of chromous and ferrous halides. On raising the temperature some or all of these halides vapourise. The chromous halide reacts with exposed ferrous metal, chromising the ferrous metal and forming ferrous halide. The ferrous halide reacts with the chromium rich layer depositing iron in this layer and forming more chromous halide. Thus, the halogen is used repeatedly in the chromising process, as in the known pack process. However, since the source of chromium is already bonded to the substrate surface, the iron deposited in the chromium is not wasted, as in the pack process and those processes in which ferrous chloride is removed from the furnace, but forms an integral part of the final alloy layer on the substrate surface. The chemical 'ferrising' of the original chromium layer in the process of this invention aids the thermal ferrising which is also taking place in the chromising operation, since it leads to more rapid formation of the chromium/iron alloy layer. If our belief as to the mechanism of the process is true, it is this factor which enables the process to operate at a lower temperature than the known processes. The role of ferrous chloride in bringing about chemical ferrising has not hitherto been appreciated and in the known processes where a non-oxidising gas is continuously passed through the furnace during chromising, such chemical ferrising is not possible and the advantages of the process of this invention cannot be realised.

In carrying out the invention, the ferrous metal substrate is first degreased and pickled and is then coated with a chromium-containing coating. The substrate may be mild steel, stainless steel or high carbon steel and may be in the form of shaped articles or, alternatively, in the form of sheet or strip material. The coating is one which contains chromium in a form which is capable of reacting with the halogen content of the vapour present in the furnace in stage 2 of the process. It may be in the form of chromium metal or an alloy thereof, for example ferro-chrome. The coating may also contain other metals which it is desired

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to incorporate in the coating of the substrate, for example nickel and aluminium.

5 The term adherent is used herein to mean that the coating must be sufficiently adherent to the surface of the ferrous metal substrate to enable it to be handled during transfer from the coating operation to the furnace, or, in the case of steel strip, to permit the strip to be coiled without the coating becoming detached. The chromium-containing coating may be deposited upon the surface of the substrate by any of the well known methods. Such methods include electrolytic deposition of chromium from conventional chromium plating solutions, plasma or flame spraying of a chromium containing powder or wire and the compaction by a rolling technique of a chromium containing powder previously distributed over the surface of the ferrous metal.

15 The amount of chromium which is initially applied in the coating of the substrates depends upon the final use to which the treated substrate is to be put and the properties desired for such an end use. For example, where mild steel is being chromised to produce a corrosion resistant coating, it is usual to provide a chromium/iron alloy layer on the surface of the mild steel which is 0.002 to 0.003 inches thick. In applications where the mild steel is to be drawn or formed after chromising, it is desirable that the coating should not have too high a chromium content. For such applications a layer containing approximately 30% chromium is desirable. To obtain such a layer 0.002—0.003 ins. thick an initial coating must be applied to the substrate at a rate of from 11 to 17 grammes of chromium per sq. ft. of the surface of the substrate. However, as indicated earlier, the initial coating of the substrate must be porous in order to permit diffusion of the chromous and ferrous halide vapours therethrough. The porosity depends to a large extent upon the thickness of the coating and the method by which it is applied to the substrate. Thus, if the chromium is electrolytically deposited upon the substrate the maximum thickness which may be deposited without serious loss of porosity is of the order of 0.001 inches. Where the chromium is applied as a powder of size 200 mesh BS and this powder is compacted upon the substrate by a rolling operation, the coating may be up to 0.003 inches thick. Thus, where a particular rate of deposition of chromium on the surface of the substrate is required, the method used to achieve this coating is determined by whether or not the particular method produces a coating which is porous enough to facilitate diffusion of the chromous and ferrous halides therethrough. However, we have found that, in general, the application

of a coating which is from 0.0001 to 0.001 inches thick provides a satisfactory result with a variety of coating methods.

The coated substrate is then subjected to a first heating stage (stage 2) in a furnace having a non-oxidising atmosphere containing a hydrogen halide. In order to obtain the non-oxidising atmosphere, it is preferred to purge the furnace of oxygen before commencing the heating operation by passing therethrough a non-oxidising gas. The non-oxidising gas may be hydrogen, argon or other inert gases. The hydrogen halide may be introduced into the furnace atmosphere either directly as the anhydrous gaseous acid or by passing the non-oxidising component of the atmosphere through an aqueous solution of the acid and subsequently drying the gas before it enters the furnace. Alternatively the halogen may be introduced with hydrogen into the furnace. The hydrogen halide may on the other hand be generated by a compound which dissociates on heating to form a hydrogen halide. For example, there may be included in the furnace charge an ammonium or other halide which decomposes on heating to give the hydrogen halide. It is preferred that the hydrogen halide employed be hydrogen chloride or hydrogen bromide.

The temperature at which the first heating stage is carried out, as indicated above, is that at which reaction between hydrogen halide and the chromium and/or exposed iron on the surface of the substrate would occur but below that at which any appreciable amount of the halides formed would be removed therefrom by evaporation. In practice we have found that this temperature lies within the range 400° to 700°C, preferably at about 600°C. The furnace is maintained at this temperature while the passage of non-oxidising gas is continued with the addition of a hydrogen halide. The amount of hydrogen halide in the gas stream and the rate of passing of the gas stream through the furnace are preferably adjusted so that there is little or no hydrogen in the furnace off-gases.

The incorporation of hydrogen halide in the furnace atmosphere is continued until sufficient halogen has been fixed on the surface of the substrate to ensure that a satisfactory speed of chromising in the stage 3 of the process of the invention is achieved. The amount of hydrogen halide incorporated will generally vary from about 30% to 60% preferably 50 to 60% of the theoretical amount of hydrogen halide required to react with all the chromium in the coating.

When the desired amount of halogen has been introduced into the furnace, the flow of gases therethrough is stopped, preferably in such a manner that the furnace remain under a slight positive pressure in order to

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minimise the possibility of leakage in of air, which might cause oxidation of the chromium or the chromous and ferrous halides.

5 In stage 3 of the process the temperature of the furnace is raised to a temperature at which chromising occurs. This temperature is in excess of 750°C and is preferably at least 800°C. Although there is no set upper limit at which chromising may occur, in practice the upper limit is set by the nature of the chromium coating applied to the substrate and the nature of the substrate itself. The temperature at which chromising takes place should not be sufficiently high to cause distortion of the substrate and/or coating, or to cause appreciable damage by overheating. We have found that chromising within the temperature region of from 800 to 1000°C usually provides a satisfactory result. Heating at this raised temperature is continued for as long a period as is required to alloy all the chromium in the coating with the ferrous metal surface. This period may be from 4 to 70 hours and decreases with increasing temperature. The composition and thickness of the chromium iron alloy in the surface of the substrate may be varied by controlling the temperature and/or time of chromising. Thus, a corrosion resistant coating on mild steel having a thickness of 0.002 to 0.003 inches and containing approximately 30% chromium may be achieved by carrying out the chromising at 800°C for a period of about 36 hours. Alternatively, coatings containing 80 to 90% chromium and only 0.0005 inches thick may be obtained by carrying out the chromising at 750°C for approximately 36 hours.

40 When the chromising has been completed to the desired extent, the residual halogen compounds in the furnace atmosphere may be removed from the furnace by purging with a non-oxidising gas before the furnace is cooled. Alternatively the furnace may be allowed to cool and the residual halides removed from the surface of the treated substrate by washing, for example with water. The treated substrate possesses a chromium/iron alloy surface whose depth and chromium content will vary with the chromising conditions employed. This coating is insoluble in boiling 50% nitric acid. Where surface coatings containing a high proportion of chromium have been obtained, such coatings have a bright appearance, particularly when the initial chromium coating of the substrate has been obtained by electro-deposition.

60 The invention will now be illustrated by the following examples.

#### EXAMPLE 1

20 gauge 0.2% carbon steel sheet is degreased by immersion in an alkaline cleaner

and is then treated anodically in 50% sulphuric acid for 30 seconds at a current density of 400 A./sq.ft. The sheet is transferred to a catalysed chromic acid chromium plating bath and a current of 300 A./sq.ft. is passed until a layer of chromium 0.0003 in. thick has been deposited. The coated sheet is washed and dried and loaded into a suitable furnace. The furnace is purged with hydrogen and heated to 600°C. A quantity of chlorine equivalent to 60% of that theoretically required to react with the chromium in the coating is injected into the hydrogen purge, over a period of 6 hours. The flow of gases is then stopped and the furnace is heated to 800°C and maintained at this temperature for 36 hours. After cooling, the sheet is removed from the furnace. The surfaces are silver-grey in colour and are resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, etc., even after bending, etc. Removal of a portion of the coating by filing and treatment with 50% aqueous nitric acid to dissolve the steel core reveals a coating insoluble in nitric acid of 0.0009 in. thickness. Analysis of the coating after dissolution in hydrochloric acid shows an iron content of 71%.

#### EXAMPLE 2

0.2% carbon steel sheet is pickled and degreased as in Example 1 and plated with chromium 0.0012 in. thick. The sheet is then heat treated as in Example 1 for 36 hours. A chromised coating 0.0021 in. thick, containing 52% Fe is obtained.

#### EXAMPLE 3

20 gauge 0.2% carbon steel sheet is degreased and pickled as in Example 1 and plated with chromium 0.0004 in. thick. The sheet is then heat treated as in Example 1 except that the final stage of the heat treatment is one of 36 hours duration at 750°C. A chromised coating 0.0004 in. thick containing 12.7% iron is obtained.

#### EXAMPLE 4

20 gauge 0.2% carbon steel sheet is degreased, pickled and plated with 0.0003 in. chromium. Portions of the sheet are chromised, using 33% and 47% respectively of the theoretical quantity of hydrogen chloride required to react with the chromium. The final stage of the heat treatment is one of 36 hours duration at 800°C. Coatings of thickness of approximately 0.0003 in. containing 3.3% and 10% iron respectively are obtained.

#### EXAMPLE 5

20 gauge 0.2% carbon steel sheet is degreased electrolytically in an alkaline cleaner and pickled in 10% v/v nitric acid for 10

seconds chromium metal powder (200 BS mesh) is applied to the surface at the rate of 16.5 g/sq. foot and this is compacted on to the surface by passing the sheet between rolls. The strip is then chromised as in Example 1. On removing the sheet from the furnace it is found that a chromised coating 0.0034 in. thick containing 62% iron has been formed.

A similar sample of steel coated with 31.8 g/sq.ft. chromium powder which is subsequently compacted by rolling, and then the coated sheet chromised under identical conditions, gives a chromised coat 0.003 in. thick containing 16% iron.

#### EXAMPLE 6

20 gauge 0.2% carbon steel sheet is cleaned and pickled as in Example 5. A quantity of 200 mesh BS chromium powder is applied to the surface of the strip sufficient to give a coating after compacting by passing the strip between rolls of 0.00045 in. thickness. The steel sheet is then loaded into the furnace and after purging and heating to 600°C a quantity of bromine equivalent to 80% of that required to react with all the chromium is injected with hydrogen into the furnace. The flow of gases is then stopped and heat treatment is carried out at 800°C for 36 hours. A chromised coating 0.0008 in. thick containing 59% iron is obtained.

#### EXAMPLE 7

0.8% carbon steel sheet is degreased and pickled as in Example 1 and plated with chromium to a thickness of 0.00015 in. The sheet is then chromised as in Example 1. A chromised coating 0.00043 in. thick containing 61.2% iron is formed.

#### EXAMPLE 8

18/8 stainless steel sheet is degreased and pickled, patted with chromium to a thickness of 0.0003 in., and chromised as in Example 1. On removing the chromised stainless steel from the furnace it is found that enhanced resistance to high temperature oxidation has been obtained. On subjecting pieces of the original stainless steel, the chromium plated stainless steel and the chromised stainless steel to air at 800°C for 7 hours, the samples showed weight gains of 0.38, 0.04 and 0.00 g. per sq.ft. of surface respectively.

#### WHAT WE CLAIM IS:—

1. A process for the chromising of ferrous metal substrates which comprises:

1. applying a porous adherent chromium-containing coating which contains chromium and optionally other metals as well to a ferrous metal substrate;

2. heating the coated substrate in a stream of a non-oxidising gas containing a hydrogen halide to a temperature which is such that the hydrogen halide reacts with the surface of the coated substrate and yet is below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation; and

3. subsequently stopping the flow of gas and heating the coated substrate to a temperature of at least 750°C for sufficient time to cause the coating of the desired thickness and composition to be formed.

2. A process according to Claim 1 wherein the non-oxidising gas is hydrogen or an inert gas.

3. A process according to either of Claims 1 and 2 wherein the coated substrate is heated in a stream of a non-oxidising gas containing a hydrogen halide to a temperature of from 400 to 700°C.

4. A process according to Claim 3 wherein the temperature is about 600°C.

5. A process according to any of the preceding claims wherein the hydrogen halide is hydrogen chloride or a precursor thereof.

6. A process according to any of the preceding claims wherein the amount of hydrogen halide fed to the furnace is from 30 to 60% of the theoretical amount required to react with all the chromium in the coating on the substrate.

7. A process according to Claim 6 wherein the amount of hydrogen halide is from 50 to 60% of the theoretical amount.

8. A process according to any of the preceding claims wherein the chromising is carried out at a temperature of from 800°C to 1000°C.

9. A process according to any of claims 1 to 8 wherein the porous adherent chromium-containing coating is applied to the ferrous metal substrate by electrolysis and is up to 0.001 inches thick.

10. A process according to any of claims 1 to 7 wherein the chromium-containing coating is applied to the substrate by applying a chromium or chromium alloy powder to the surface of the ferrous metal substrate and subsequently compacting this powder upon the substrate by means of a rolling technique.

11. A process according to claim 10 wherein the chromium powder applied to the substrate has a particle size of 75 microns or less and the coating is up to 0.003 inches thick.

12. A process according to any of the preceding claims wherein the substrate is in the form of sheet or strip material.

13. A process according to any of the

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preceding claims wherein the chromium-containing coating of the substrate also contains nickel or aluminium.

5 14. A process for the chromising of ferrous metal substrates substantially as hereinbefore described in the Examples.

15. Ferrous metal substrates whenever

chromised by a process as claimed in any of claims 1 to 14.

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